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(54) Title: FLUORESCENT SECURITY INKS AND MARKERS COMPRISING CARBON NANOTUBES



(57) Abstract: The present invention is directed toward fluorescent inks and markers comprising carbon nanotubes. The present invention is also directed toward methods of making such inks and markers and to methods of using such inks and markers, especially for security applications (e.g., anti-counterfeiting). Such inks and markers rely on the unique fluorescent properties of semiconducting carbon nanotubes.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

FLUORESCENT SECURITY INKS AND MARKERS COMPRISING CARBON NANOTUBES

[0001] The present invention was made with support from the Robert A. Welch Foundation, Grant No. C-0807; and the National Science Foundation, Grant No. CHE-9900417.

CROSS REFERENCE TO RELATED APPLICATIONS

[0002] This Application claims priority to United States Provisional Patent Application Serial No. 60/500,394, filed September 5, 2003.

FIELD OF THE INVENTION

[0003] The present invention relates generally to fluorescent inks and markers, especially for security applications. More specifically, the invention relates to such inks and markers comprising carbon nanotubes.

BACKGROUND OF THE INVENTION

[0004] The issues of authentication and counterfeit deterrence can be important in many contexts. Bills of currency, stock and bond certificates, credit cards, passports, driver's licenses, as well as many other legal documents (e.g., deeds, wills, etc.) all must be reliably authentic to be useful. Museums and art galleries face such challenges when authenticating works of art. Additionally, consumer products and other articles of manufacturing, such as pharmaceuticals, books, movies, software, etc., are frequently the subject of counterfeiting in the form of "pirated" versions or "knock-offs."

[0005] A wide variety of attempts have been made to limit the likelihood of counterfeiting. Most such attempts tend to incorporate a unique identifier into the potentially counterfeited item. The addition of fluorescent compounds to inks and dyes has long been a technique used by governments and banks for anti-counterfeiting purposes. Likewise, fluorescent compounds can be incorporated or

otherwise associated with other articles for identification and/or anti-piracy purposes. See, e.g., United States Patent Nos. 4,558,224 and 6,246,061.

[0006] Fluorescence, being a subset of photoluminescence (PL), occurs when a material is irradiated with electromagnetic radiation (EM), at least some of which is absorbed. Fluorescence refers to the subsequently re-emitted radiation of wavelength other than that which was absorbed. Typically, such emission, or fluorescence, is red-shifted to longer wavelengths relative to the incident or absorbed radiation, such emission can also be described as being Stokes shifted. The terms "fluorescence," "luminescence," and "photoluminescence," will be used synonymously herein.

[0007] Fluorescent compounds typically used in such above-described applications are generally organic molecules that fluoresce in the visible region of the EM spectrum when irradiated with ultra-violet (UV) light. There is, however, a constant need for both new and better fluorescent compounds to a) stay ahead of the would-be counterfeiters, and b) to expand the breadth of such marking and authentication techniques, wherein such fluorescent compounds offer a more unique optical signal and/or yield themselves to processing and operating conditions unsuitable for existing fluorescent compounds.

BRIEF DESCRIPTION OF THE INVENTION

[0008] The present invention is directed toward fluorescent inks and markers comprising carbon nanotubes, and to methods of using carbon nanotubes (CNTs) as fluorescent identifiers for anti-counterfeiting and authentication purposes.

[0009] Generally, the fluorescent inks of the present invention comprise a dispersion or suspension of CNTs in a liquid (i.e., solvent) medium. Such a dispersion may further comprise surfactant species and/or other traditional ink components. Such inks may be referred to herein as "nanotube inks." Note that such inks are but a subset of the fluorescent markers of the present invention that can be attached to, incorporated into, or otherwise associated with an article for which identification and/or authentication is deemed important, generally at some point in the future.

[0010] Methods of using CNTs as fluorescent identifiers generally rely on a knowledge of their photoluminescence properties and on techniques of incorporating and/or attaching such species into and/or to articles being marked or tagged. Note that the terms "marker" and "taggant" (and their verb conjugates) will be used synonymously herein.

[0011] Generally, the fluorescence is effected by irradiating the item or article comprising CNTs with visible light (i.e., radiation in the visible region of the EM spectrum). The fluorescence is then detected in the near infrared (NIR) region of the EM spectrum. Depending on the embodiment, such detection can be of a qualitative or quantitative nature. In some embodiments, the detection involves imaging. Such imaging can be spectral or even multi-spectral.

[0012] In some embodiments of the present invention, the CNTs are chemically derivatized. Such chemical derivatization expands the range of solvents and solvent systems that can be employed to generate the suspension of single-wall carbon nanotubes as utilized in the present invention. Such chemical derivatization can be removed via thermal and/or chemical treatments subsequent to printing such inks and/or incorporating such markers.

[0013] In some embodiments, the CNTs are homogenized by electronic type according to a separation procedure. Generally, this translates to a concentration of one electronic type within a mixture of types (e.g., increasing the amount of semiconducting CNTs with respect to metallic and semi-metallic CNTs). Thus, in some embodiments, the population of CNTs for a particular application may be largely semiconducting CNTs with a small range of bandgaps.

[0014] In some embodiments, through such above-described chemical derivatizations and/or separation procedures, "designer" compositions of CNTs can be used in which the photoluminescence properties of the CNT-based inks and markers are tuned within a range of excitation and emission wavelengths. This provides for an almost limitless variety of unique inks and markers with which to incorporate into, and/or associate with, articles for identification, anti-counterfeiting, and authentication purposes. In some embodiments, the fluorescence characteristics of a population of CNTs is varied by modulating the parameters of the CNT synthesis.

[0015] In some embodiments, the invention is drawn to a suspension of CNTs, such as a suspension of single-walled carbon nanotubes (SWNTs), wherein the suspension serves as an invisible ink. In some embodiments, this ink is an aqueous suspension. When dried, this nanotube ink is virtually invisible. However, the nanotube ink will fluoresce when illuminated with light of an appropriate wavelength; for instance it will glow in the near-infrared when illuminated with visible light of the appropriate wavelength. If partly or fully structure-separated nanotube samples are used, then one can prepare inks that have distinct wavelengths of excitation and emission.

[0016] In some embodiments of the present invention, a dilute aqueous surfactant suspension of CNTs, such as SWNTs, is applied to paper or cloth using flowing ink pens, inkjet printers, etc., wherein such a suspension (dispersion) is the ink. After drying, the "ink" can be illuminated with visible light matching a second, third, or higher van Hove optical transition of the semiconducting carbon nanotubes. This yields a luminescence emission at a corresponding first van Hove wavelength in the near-infrared. Resulting images (in the case of written words, shapes, and/or patterns) can be visualized in the near-infrared using appropriate near-infrared detection equipment (e.g., an InGaAs camera). Spectral filtering can also distinguish different nanotube species in the ink, because each will show distinct absorption and emission wavelengths. This latter aspect is highly relevant in embodiments wherein pluralities of nanotubes have been manipulated to be concentrated in a particular type species within the greater collection of CNTs within the ink or marker.

[0017] In some embodiments, the compositions (inks and markers) of the present invention are used as anti-counterfeiting markings for high-value items, such as currency. Nanotubes of different diameters can be used to prepare various inks for selectively inscribing different denominations of bills. For example, a \$100 bill would exhibit fluorescence only with a specific combination of excitation and observation wavelengths; a \$50 bill with a different combination, etc. This spectral selectivity feature can be used with or without imaging detection.

[0018] In some embodiments, the compositions and methods of the present invention are used to provide spectral "bar coding" for non-contact identification of items, such as clothing. Combinations of different nanotube inks can be applied to merchandise at the factory and then detected remotely by an infrared scanner for

inventory-taking, identification at a sales counter, or theft control. The selective use of several different nanotube species provides many possible combinations of emission wavelengths that can be used to generate spectral bar code identifiers.

[0019] In some embodiments, the compositions of the present invention are used in currency as replacements for the magnetic identifiers currently used to identify different denominations (such as by integration of the nanotube inks into the currency), in machines, such as, for example, vending machines. Such an application would rely on optical detection rather than magnetic detection to differentiate the bills. Alternatively, such optical identifiers of the present invention can be used in combination with existing identifiers (e.g., magnetic materials and/or fluorescent dyes). Numerous other applications for such inks/markers exist.

[0020] The present invention provides improvement over the existing fluorescent identifiers in that the unique excitation and emission wavelengths of these nanotube inks and markers cannot be simulated by conventional fluorescent materials. Furthermore, the region of the EM spectrum in which these inks and markers fluoresce is generally inaccessible with other fluorophores. Also, there is virtually no background emission in the near-infrared, so only tiny quantities of nanotubes are required for marking. Furthermore, other fluorescent ink materials do not offer the variety of wavelength-specific forms that can provide the added information and security of nanotube ink. Finally, numerous methods of inducing luminescence and known detection systems capable of detecting the emission can be employed.

[0021] The foregoing has outlined rather broadly the features of the present invention in order that the detailed description of the invention that follows may be better understood. Additional features and advantages of the invention will be described hereinafter which form the subject of the claims of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] For a more complete understanding of the present invention, and the advantages thereof, reference is now made to the following descriptions taken in conjunction with the accompanying drawings, in which:

[0023] FIGURE 1 is a fluorescence spectral analysis of an aqueous (D_2O) suspension of SWNTs obtained using a single-wavelength excitation (651 nm), wherein the SWNTs are surfactant-suspended with sodium dodecylsulfate (SDS), and wherein a deconvolution of the peaks illustrates the manner in which the fluorescence is highly unique to a particular collection of CNTs such that each one of the deconvoluted peaks in the figure is the result of a different semiconducting SWNT species being present, the particular species being indicated by the n,m indices above each peak;

[0024] FIGURE 2 depicts fluorescence spectra of two batches of SWNTs produced by the same reactor, but under slightly different synthesis conditions, that yield different fluorescence signatures when irradiated with 660 nm radiation from a diode laser source, wherein the relative quantities of particular SWNT semiconducting species within Batch 1 (dashed line) differ from those within Batch 2 (solid line);

[0025] FIGURE 3 illustrates a near-infrared photograph of an embodiment wherein single-wall carbon nanotubes are applied to a surface (as ink) and illuminated with light in the visible region to effect photoluminescence in the near-infrared;

[0026] FIGURE 4 is a fluorescence spectrum of SWNT fluorescence markers that have been integrated into a PMMA host, wherein excitation is at 669 nm from a diode laser; and

[0027] FIGURE 5 depicts the fluorescence spectra of a single sample of SWNT (HiPco, Rice University), taken with three different excitation wavelengths, wherein excitation wavelengths are as follows: trace a, 669 nm; trace b, 573 nm; and trace c, 723 nm.

DETAILED DESCRIPTION OF THE INVENTION

[0028] The present invention is directed toward fluorescent inks and markers comprising carbon nanotubes, and to methods of using carbon nanotubes (CNTs) as fluorescent identifiers for anti-counterfeiting and authentication purposes.

[0029] Carbon nanotubes (CNTs) comprising multiple concentric shells and termed multi-wall carbon nanotubes (MWNTs) were discovered by Iijima in 1991 [Iijima, *Nature* **1991**, 354, 56]. Subsequent to this discovery, single-wall carbon nanotubes (SWNTs), comprising a single graphene rolled up on itself, were synthesized in an arc-discharge process using carbon electrodes doped with transition metals [Iijima, S.; Ichihashi, T. *Nature* **1993**, 363, 603; and Bethune *et al.* *Nature* **1993**, 363, 605]. These carbon nanotubes (especially CNTs with diameters less than about 3 nm, e.g., SWNTs) possess unique mechanical, electrical, thermal and optical properties, and such properties make them attractive for a wide variety of applications. See Baughman *et al.*, *Science*, **2002**, 297, 787-792.

[0030] The diameter and chirality of individual CNTs are described by integers "n" and "m," where (n,m) is a vector along a graphene sheet which is conceptually rolled up to form a tube. When $|n-m| = 3q$, where q is an integer, the CNT is a semi-metal (bandgaps on the order of milli eV). When $n-m = 0$, the CNT is a true metal and referred to as an "armchair" nanotube. All other combinations of n-m are semiconducting CNTs with bandgaps typically in the range of 0.5 to 1.5 eV. See O'Connell *et al.*, *Science*, **2002**, 297, 593. CNT "type," as used herein, refers to such electronic types described by the (n,m) vector (*i.e.*, metallic, semi-metallic, and semiconducting). CNT "species," as used herein, refers to CNTs with discrete (n,m) values. It is the semiconducting CNTs that possess fluorescence properties that make them useful as the optical identifiers of the present invention.

[0031] All known preparative methods lead to polydisperse materials of semiconducting, semimetallic, and metallic electronic types. See M. S. Dresselhaus, G. Dresselhaus, P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes*, Academic Press, San Diego, 1996; Bronikowski *et al.*, *Journal of Vacuum Science & Technology* **2001**, 19, 1800-1805; R. Saito, G. Dresselhaus, M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes*, Imperial College Press, London, 1998. As such, a primary hurdle to the widespread application of CNTs, and SWNTs in particular, is their manipulation according to electronic structure [Avouris, *Acc. Chem. Res.* **2002**, 35, 1026-1034].

[0032] Recent advances in the solution phase dispersion [Strano *et al.*, *J. Nanosci. and Nanotech.*, **2003**, 3, 81; O'Connell *et al.*, *Science*, **2002**, 297, 593-596] along with spectroscopic identification using bandgap fluorescence [Bachilo *et al.*,

Science, **2002**, 298, 2361; and commonly-assigned United States Patent Application Serial No. 10/379,273] and Raman spectroscopy [Strano, *Nanoletters* **2003**, 3, 1091] have greatly improved the ability to monitor electrically distinct nanotubes as suspended mixtures and have led to definitive assignments of the optical features of semiconducting [Bachilo *et al.*, *Science*, **2002**, 298, 2361], as well as metallic and semi-metallic species [Strano, *Nanoletters*, **2003**, 3, 1091]. Indeed, such spectroscopic assignments can provide a background for the optical bar coding of the present invention.

[0033] Shown in FIGURE 1 is a fluorescence spectral analysis of an aqueous (D_2O) suspension of SWNTs using a single-wavelength excitation (651 nm), wherein the SWNTs are surfactant-suspended with sodium dodecylsulfate (SDS). Deconvolution of the peaks illustrates the manner in which the fluorescence is highly unique to a particular collection of CNTs. Each one of the deconvoluted peaks in the figure is the result of a different semiconducting SWNT species being present, the particular species being indicated by the n,m indices above each peak. Emission intensity for each peak is a function of the relative concentration of the particular species providing for a particular peak.

[0034] Techniques of chemically functionalizing CNTs have greatly facilitated the ability to manipulate these materials, particularly for SWNTs which tend to assemble into rope-like aggregates [Thess *et al.*, *Science*, **1996**, 273, 483-487]. Such chemical functionalization of CNTs is generally divided into two types: tube end functionalization [Chen *et al.*, *Science*, **1998**, 282, 95-98], and sidewall functionalization [PCT publication WO 02/060812 by Tour *et al.*; Holzinger *et al.*, *Angew. Chem. Int. Ed.*, **2001**, 40, 4002-4005; Khabashesku *et al.*, *Acc. Chem. Res.*, **2002**, 35, 1087-1095]. Most recently, SWNTs were shown to be selectively functionalizable, providing a chemical route to their separation. See Strano *et al.*, *Science*, **2003**, 301, 1519-1522; and commonly-assigned International Patent Application No. PCT/US04/24507.

[0035] Carbon nanotube chemistry has been described using a pyramidization angle formalism [S. Niyogi *et al.*, *Acc. of Chem. Res.*, **2002**, 35, 1105-1113]. Here, chemical reactivity and kinetic selectivity are related to the extent of s character due to the curvature-induced strain of the sp^2 -hybridized graphene sheet. Because strain energy per carbon is inversely related to nanotube diameter, this model predicts

smaller diameter nanotubes to be the most reactive, with the enthalpy of reaction decreasing as the curvature becomes infinite. While this behavior is most commonly the case, the role of the electronic structure of the nanotubes in determining their reactivity is increasingly important—especially when desiring selectivity among a population of similar-diameter CNTs (such as is often the case with SWNT product). Furthermore, because such structure is highly sensitive to chiral wrapping, chemical doping, charged adsorbates, as well as nanotube diameter, there exists a considerable diversity among these various pathways in addition to a simple diameter dependence, and with implications for separating CNTs by type.

[0036] Other methods with which CNTs can be separated by type have been reported. Such techniques include dielectrophoresis [Krupke *et al.*, *Science*, **2003**, 301, 244-347], selective precipitation [Chattopadhyay *et al.*, *J. Am. Chem. Soc.*, **2003**, 125, 3370-3375], ion-exchange chromatography [Zheng *et al.*, *Nature Mater.*, **2003**, 2, 338-342], and complexation/centrifugation [Chen *et al.*, *Nano Lett.*, **2003**, 3, 1245-1249].

[0037] Carbon nanotubes (CNTs), according to the present invention, include, but are not limited to, single-wall carbon nanotubes (SWNTs), multi-wall carbon nanotubes (MWNTs), double-wall carbon nanotubes, buckytubes, fullerene tubes, tubular fullerenes, graphite fibrils, and combinations thereof. Such carbon nanotubes can be of a variety and range of lengths, diameters, number of tube walls, chiralities (helicities), etc., and can be made by any known technique including, but not limited to, arc discharge [Ebbesen, *Annu. Rev. Mater. Sci.* **1994**, 24, 235-264], laser oven [Thess *et al.*, *Science* **1996**, 273, 483-487], flame synthesis [Vander Wal *et al.*, *Chem. Phys. Lett.* **2001**, 349, 178-184], chemical vapor deposition [United States Patent No. 5,374,415], wherein a supported [Hafner *et al.*, *Chem. Phys. Lett.* **1998**, 296, 195-202] or an unsupported [Cheng *et al.*, *Chem. Phys. Lett.* **1998**, 289, 602-610; Nikolaev *et al.*, *Chem. Phys. Lett.* **1999**, 313, 91-97] metal catalyst may also be used, and combinations thereof. While not intending to be bound by theory, it is believed that the CNTs exhibiting photoluminescence in accordance with the present invention typically have diameters less than about 3 nm.

[0038] Depending on the embodiment, the CNTs can be subjected to one or more processing steps. In some embodiments, the CNTs have been purified. Exemplary purification techniques include, but are not limited to, those by Chiang *et al.* [Chiang

et al., *J. Phys. Chem. B* **2001**, *105*, 1157-1161; Chiang *et al.*, *J. Phys. Chem. B* **2001**, *105*, 8297-8301]. In some embodiments, the CNTs have been cut by a cutting process. See Liu *et al.*, *Science* **1998**, *280*, 1253-1256; Gu *et al.*, *Nano Lett.* **2002**, *2*(9), 1009-1013; Haddon *et al.*, *Materials Research Society Bulletin*, **2004**, *29*, 252-259. The terms "carbon nanotube" and "nanotube" will be used interchangeably herein.

[0039] Depending on the embodiment, the CNTs used in the inks, markers, and methods of the present invention can be separated by length, diameter, type or species and/or chemically derivatized according to any of the above-described separation and/or chemical derivatization methods. "Separation," as defined herein, generally involves the concentration of CNTs of a particular type, dimension, or species. The extent of such separation, and the level at which it is carried out, can lead to essentially homogeneous populations of CNTs comprising a particular type, dimension, or species of CNT.

[0040] Generally, the fluorescent inks of the present invention ("nanotube inks") comprise a dispersion or suspension of CNTs in a liquid (*i.e.*, solvent) medium. Such a dispersion may further comprise surfactant species and/or other traditional ink components. Fluorescent markers of the present invention are simply compositions CNTs with established photoluminescent properties that can be attached, incorporated into, and/or otherwise associated with an article for the purpose of identification and/or authentication. In some embodiments, the marker compositions may further comprise material other than CNTs, *e.g.*, polymer.

[0041] In some embodiments, the CNTs within a nanotube ink or marker have been homogenized or separated by one or more of the above-described techniques. In some embodiments, separation and/or chemical derivatization techniques, such as those described above, are used to generate unique, designer mixtures of nanotubes of varying type, dimension and/or species. In some embodiments, it is merely enough to predetermine the fluorescence properties of the CNT mixture in a qualitative or quantitative manner. In some embodiments, the process parameters for the synthesis of the CNTs are altered so as to produce CNTs with a slightly different fluorescence signature. Indeed, there is greater flexibility for unique fluorescence signatures from mixtures than from homogenous populations (of CNTs). Referring to FIGURE 2, it can be seen that SWNTs produced by the same

reactor, but under slightly different synthesis conditions, yield different fluorescence signatures when irradiated with 660 nm radiation from a diode laser source, wherein the relative quantities of particular SWNT semiconducting species within Batch 1 (dashed line) differ from those within Batch 2 (solid line).

[0042] Suitable solvent media for nanotube inks and markers include, but are not limited to, water, alcohols, alkanes, *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), *o*-dichlorobenzene, benzene, xylenes, toluene, mesitylene, tetrahydrofuran, chloroform, dichloromethane, FREONs (general class of halocarbons, primarily fluorinated hydrocarbons), supercritical fluids (SCFs, such as supercritical CO₂), and combinations thereof.

[0043] Surfactants, according to the present invention, can be any chemical agent which facilitates the dispersion of carbon nanotubes in water or other solvent media. Surfactants include ionic (cationic and anionic) surfactants and non-ionic surfactants. Suitable surfactants include, but are not limited to, sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfonate (SDBS), sodium octylbenzene sulfonate, TRITON X-100, TRITON X-405, dodecyltrimethylammonium bromide (DTAB), and combinations thereof. Such surfactants can aid in maintaining the stability of the dispersion and/or facilitating the wetting of a surface by the nanotube ink.

[0044] In some embodiments, the CNTs are dispersed in a superacid (e.g., oleum) or other intercalating media. See Ramesh *et al.*, *J. Phys. Chem. B*, **2004**, *108*, 8794-8798.

[0045] In some embodiments, the CNTs, as markers, are incorporated into a polymer host as a composite or blend material, wherein the CNTs have a predetermined fluorescence signature. This blend can then be used to fabricate articles of manufacture, objects, or parts. In some embodiments, polymer fibers comprising such CNT fluorescence markers are fabricated. Such fibers can be used to make paper, currency, textiles, etc. Generally, but not always, the material or article into which the CNT fluorescence markers are being blended should be transparent to both the excitation and emission wavelengths used to detect and analyze the fluorescence signature.

[0046] Methods of using the fluorescent nanotube inks of the present invention can generally comprise the steps of: 1) depositing a suspension of CNTs onto a

surface, generally in the form of words, shapes, and/or patterns, and 2) removing the solvent. Provided that relatively small quantities of the CNTs are actually transferred to the surface, such words, shapes, and/or patterns can be said to be invisible and the nanotube ink referred to as an invisible ink. Such methods typically also can comprise the steps of 3) irradiating the ink with a visible light source, and 4) viewing the resulting fluorescence with a NIR optical viewer, such as an InGaAs camera or other such device.

[0047] As above, CNTs within such a suspension (dispersion) may previously have been subjected to separation and/or chemical derivatization techniques to generate homogenous and/or designer mixtures of CNTs. In some embodiments, where the CNTs have been subjected to chemical derivatization, a further step of thermal and/or chemical defunctionalization is used to cause the CNTs to revert back to their original underivatized state [Bahr *et al.*, *J. Mater. Chem.*, **2002**, 12, 1952-1958]. Depending on the embodiment, and for use as an ink, it is generally sufficient to merely have a qualitative knowledge of the fluorescent properties of the CNTs within the mixture, such that no manipulation of the CNTs by type, dimension (length, diameter), or species is necessary for their use as inks.

[0048] The suspension of CNTs generally has the CNTs dispersed in a suitable solvent medium. As described above, there is considerable variety in the selection of such media. Often, a surfactant is added to provide for or enhance the suspension of CNTs.

[0049] In some embodiments of the present invention, the process of forming a mixture of surfactant-suspended carbon nanotubes comprises a homogenizing step. A homogenizing step, according to the present invention, can be any method which suitably homogenizes the mixture and renders at least some of the carbon nanotubes encapsulated in micellar-like assemblies.

[0050] In some embodiments of the present invention, the process of forming an mixture of surfactant-suspended carbon nanotubes further comprises ultrasonic assistance. Ultrasonic assistance can be provided by either an ultrasonic bath or an ultrasonic horn sonicator, typically operating at a power from between about 200 W to about 600 W. The duration of such ultrasonic assistance typically ranges from about 1 min to about 20 min.

[0051] In some embodiments of the present invention, the mixture of surfactant-suspended carbon nanotubes is centrifuged to separate the surfactant-suspended nanotube material from other material. In such embodiments, the other material gravitates to the bottom and the surfactant-suspended carbon nanotubes are decanted. In some embodiments of the present invention, the centrifugation is provided by an ultracentrifuge, and centrifugation is performed with an intensity which ranges generally from about 10,000 rpm to about 90,000 rpm, and for a duration which ranges generally from about 1 hour to about 6 hour.

[0052] In some embodiments, one or more additional materials are added to the suspension of CNTs (the ink). Such additional materials may include, dyes, binders, traditional fluorescent inks, magnetic materials, nanoparticles, or other materials used in the formulation of inks.

[0053] Surfaces or substrates, according to the present invention, include but are not limited to, paper, natural or synthetic fibers, metals, polymeric materials, ceramics, glasses, etc. In some embodiments, the surface is pretreated to facilitate adhesion of the ink. Such pretreatments can be of a chemical (e.g., etching) or physical (e.g., plasma) nature.

[0054] Depositing the suspension of CNTs, as nanotube ink, onto a surface can be by way of any number of standard printing techniques. Such techniques include, but are not limited to, inkjet printing, screen printing, lithographic techniques, brushing, spraying, flowing ink pens, stamping, and combinations thereof.

[0055] As an ink, such deposition can generally be in some patterned form such as words and/or shapes and symbols. In some embodiments, however, this nanotube ink is invisible to the naked eye.

[0056] Solvent removal generally involves an evaporative process. Such evaporative processes can be facilitated by heat, vacuum, and/or other processes.

[0057] In some embodiments, after solvent removal, an additional treatment is applied to the deposited ink. Such additional treatments generally serve to protect the integrity of the words, shapes or symbols printed on a surface. Such treatments may comprise a lamination, e.g., the deposition of a polymer or glass film over the deposited ink, wherein the deposited polymer or glass is transparent to both the excitation and emission wavelengths required to induce and detect fluorescence.

[0058] Irradiation of the deposited ink can be done with a variety of visible light sources. Such sources provide the excitation required for fluorescence and can be monochromatic or polychromatic in nature. In some embodiments, the excitation source is a laser. In some embodiments, the excitation source has a wavelength near or above 750 nm so as to be essentially invisible itself.

[0059] Viewing or detecting the fluorescent emission, which has a frequency in the near infrared region of the EM spectrum, is generally done with an near infrared viewer or camera, such as an InGaAs camera or imager. It is generally not necessary, in the case of such inks, to resolve the spectral information, but this can be done with spectral imaging techniques when desired.

[0060] Methods of using CNTs as fluorescent identifiers (e.g., spectral bar codes) rely on a knowledge of their photoluminescence properties and on techniques of incorporating and/or attaching such species to articles being marked or tagged. Generally, such methods comprise the steps of: 1) providing a plurality of carbon nanotubes with unique, predetermined photoluminescence characteristics; and 2) incorporating the carbon nanotubes into articles as optical identifiers to form optically tagged articles. Methods of using CNTs as fluorescent identifiers may further comprise the steps of: 3) irradiating the optically tagged articles with EM radiation; and 4) detecting photoluminescence from the carbon nanotubes for the purpose of identifying the optically tagged article.

[0061] The use of CNTs compositions as markers generally requires a thorough understanding of their fluorescence properties. In some embodiments, the CNTs have been subjected to separation and/or chemical derivatization techniques to generate homogenous and/or designer mixtures of CNTs. In some embodiments, where the CNTs have been subjected to chemical derivatization, a further step of thermal and/or chemical defunctionalization is used to cause the CNTs to revert back to their original, underivatized state. In some embodiments, CNTs are synthesized as unique mixtures with unique fluorescent properties. Regardless of how the CNTs have been synthesized and/or processed, the fluorescence signature (i.e., spectra) for such CNTs is carefully evaluated (i.e., predetermined) prior to marking or tagging articles or objects with the CNT fluorescent markers.

[0062] In some embodiments, the CNT markers can be suspended in a solvent medium and applied as an ink (as above). Such inks could contain multiple levels of information, wherein the shapes and/or words contain one level of information and additional levels of spectral information can be contained within the CNT marker compositions within the inks.

[0063] In some embodiments, the markers are incorporated into a host material, wherein the host material is generally transparent to the excitation and emission wavelengths with which the CNTs fluoresce. Typically, such host materials are polymeric in nature, but they can also be ceramic or glass. The CNT markers can be attached to an article either directly or in a host material. In some embodiments, the CNTs markers are incorporated into a host material that makes up an article or manufacture. For example, CNT markers could be blended into synthetic fibers which are then used to make articles of clothing. In some embodiments, the host material is liquid or fluid.

[0064] Irradiating the CNT fluorescent markers can be done with a variety of visible light sources. Such sources provide the excitation required for fluorescence and can be monochromatic or polychromatic in nature. In some embodiments, the excitation source is a laser. Suitable lasers sources include, but are not limited to, solid state diode lasers, HeNe lasers, Ar lasers, Kr lasers, and combinations thereof. In some embodiments, greater differentiation between sets of CNTs is afforded by the use of two or more discrete excitation wavelengths.

[0065] Detection of the emission can be qualitative in nature using spectral filters and such. More typically, however, detection is such that the spectral signature of the CNT markers is resolved, thus providing a high level of identification. Such spectral resolution is typically provided via spectroscopic gratings and NIR detectors. Suitable NIR detectors include, but are not limited to, photodiodes, photomultipliers, one- or two-dimensional photodiode arrays, or CCD or CMOS cameras based on semiconductors such as Si, Ge, or InGaAs.

[0066] Applications for the nanotube inks and markers of the present invention include, but are not limited to, authentication of currency, security documents, passports, drivers licenses, pharmaceuticals, clothing and other consumer goods, books, art, and combinations thereof. Such inks and markers can be used in quality

or process control to identify batches. Such inks or markers could also be used in leak detection or other similar applications. Additionally such inks and/or markers could be used in combination with other methods of authentication and identification such as magnetic devices, strips or labels.

[0067] The following examples are provided to more fully illustrate some of the embodiments of the present invention. It should be appreciated by those of skill in the art that the techniques disclosed in the examples which follow represent techniques discovered by the inventors to function well in the practice of the invention, and thus can be considered to constitute exemplary modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments that are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention.

Example 1

[0068] This Example serves to illustrate a manner in which nanotube inks can be used according to some embodiments of the present invention.

[0069] SWNTs (HiPco, Rice University) were dispersed in an aqueous solution of SDS surfactant by an accepted process of high-shear mixing, ultrasonic agitation, and ultracentrifugation to create a nanotube ink.

[0070] The nanotube ink suspension was used to fill the reservoir of a flowing ink drafting pen, which was then used with a drafting template to write the characters "SWNT" onto a piece of office paper manufactured with a mild gloss coating. The ink was then allowed to dry such that the resulting characters were approximately 5 mm in height and with a mass per character of approximately 10 nanograms. Such a small amount of SWNTs renders the ink invisible to the naked eye.

[0071] Upon irradiation with monochromatic light of 671 nm wavelength, the letters were seen to fluoresce, emitting radiation in the NIR. This emission was detected with a camera with a detection range of 1125-1700 nm. While invisible to the naked eye, FIGURE 3 is an image generated by this NIR camera with an exposure of 6 video frames.

Example 2

[0072] This Example serves to illustrate how CNT fluorescent markers can be integrated into host materials like polymers.

[0073] SWNTs (HiPco, Rice University) were blended into a poly(methylmethacrylate) (PMMA) matrix by ultrasonic dispersion of SWNTs into a xylene solution of PMMA. Evaporation of the xylene gave an optically clear solid containing fluorescent SWNTs.

[0074] FIGURE 4 is a fluorescence spectrum of these SWNT markers which have been integrated into the PMMA host, wherein excitation is at 669 nm from a diode laser. Each peak indicated by an arrow corresponds to fluorescence from a different SWNT species within the sample.

Example 3

[0075] This Example serves to illustrate excitation selectively within a CNT sample comprising a variety of CNT species.

[0076] In the case of SWNTs, due to excitation selectivity, only a subset of SWNT types will be detectable with some "standard" excitation wavelength, such as 660 to 670 nm (the region where some common semiconductor diode lasers emit). Many nanotube types that might be present in the sample may be hidden or exhibit an emission intensity which is too low to be detected, especially where such peaks lie close to intense peaks activated with such "standard" excitation wavelengths. The application of additional excitation wavelengths can possibly reveal these typically "hidden" peaks (and the semiconducting SWNT species that produce them).

[0077] FIGURE 5 depicts the fluorescence spectra of the same SWNT sample (HiPco, Rice University), taken with three different excitation wavelengths, wherein excitation wavelengths are as follows: trace a, 669 nm; trace b, 573 nm; and trace c, 723 nm.

[0078] It can be seen from FIGURE 5 that the relative intensities of the peaks change when the excitation frequency is changed, revealing a selectivity to the

excitation. Such excitation selectivity can be exploited in anti-counterfeiting applications.

[0079] All patents and publications referenced herein are hereby incorporated by reference. It will be understood that certain of the above-described structures, functions, and operations of the above-described embodiments are not necessary to practice the present invention and are included in the description simply for completeness of an exemplary embodiment or embodiments. In addition, it will be understood that specific structures, functions, and operations set forth in the above-described referenced patents and publications can be practiced in conjunction with the present invention, but they are not essential to its practice. It is therefore to be understood that the invention may be practiced otherwise than as specifically described without actually departing from the spirit and scope of the present invention as defined by the appended claims.

WHAT IS CLAIMED IS:

1. A nanotube ink comprising a suspension of carbon nanotubes, wherein the carbon nanotubes are operable for undergoing photoluminescence and yielding emission within a pre-determined range of wavelengths when irradiated with radiation in the visible region of the EM spectrum, and wherein the nanotube ink is formulated for adhesion to a substrate surface when such a surface is printed with said nanotube ink.
2. The nanotube ink of Claim 1, wherein the carbon nanotubes are selected from the group consisting of single-wall carbon nanotubes, multi-wall carbon nanotubes, double-wall carbon nanotubes, and combinations thereof.
3. The nanotube ink of Claim 1, wherein the carbon nanotubes comprise single-wall carbon nanotubes.
4. The nanotube ink of Claim 1, wherein the carbon nanotubes comprise nanotubes having diameters less than about 3 nm.
5. The nanotube ink of Claims 1-3, or 4, wherein the carbon nanotubes within the nanotube ink are substantially homogeneous with respect to their photoluminescence properties.
6. The nanotube ink of Claims 1-3, or 4, wherein the carbon nanotubes within the nanotube ink comprise an artificially-generated population of single-wall carbon nanotubes of different nanotube species, such artificial generation provided by carbon nanotube separation techniques.
7. The nanotube ink of Claims 1-3, or 4, wherein the suspension comprises a liquid medium selected from the group consisting of water, organic solvents, supercritical fluids, and combinations thereof.
8. The nanotube ink of Claim 7, wherein the suspension further comprises surfactant.
9. The nanotube ink of Claims 1-7, or 8 further comprising an additive selected from the group consisting of traditional fluorescent inks, dyes, binders, polymeric material, nanoparticles, magnetic materials, and combinations thereof.

10. The nanotube ink of Claims 1-8, or 9, wherein the pre-determined range of wavelengths are in the near infrared.
11. A composition comprising:
 - a) a substrate; and
 - b) a plurality of carbon nanotubes in contact with said substrate, wherein said carbon nanotubes are operable for undergoing photoluminescence at a pre-determined range of wavelengths, and wherein the carbon nanotubes are part of a dried nanotube ink formulation, said nanotube ink formulated to adhere to the substrate in its dry state.
12. The composition of Claim 11, wherein the carbon nanotubes are selected from the group consisting of single-wall carbon nanotubes, multi-wall carbon nanotubes, double-wall carbon nanotubes, and combinations thereof.
13. The composition of Claim 11, wherein the carbon nanotubes comprise single-wall carbon nanotubes.
14. The composition of Claim 11, wherein the carbon nanotubes comprise nanotubes having diameters less than about 3 nm.
15. The composition of Claims 11-13, or 14, wherein the substrate comprises a fibrous material.
16. The composition of Claim 15, wherein the fibrous material is selected from the group consisting of paper, synthetic polymers, cotton, silk, and combinations thereof.
17. The substrate of Claims 11-13, or 14, wherein the substrate is a security.
18. The composition of Claims 11-13, or 14, wherein the substrate is currency.
19. A method for contacting a nanotube ink with a substrate comprising the steps of:
 - a) selecting a substrate;
 - b) selecting a nanotube ink comprising a suspension of carbon nanotubes in a liquid medium, wherein the carbon nanotubes have pre-determined photoluminescence properties, and wherein the suspension is formulated as an ink;

- c) applying said nanotube ink to said substrate; and
 - d) removing the liquid medium from the nanotube ink to leave a dried nanotube ink in contact with the substrate.
20. The method of Claim 19, wherein the carbon nanotubes are selected from the group consisting of single-wall carbon nanotubes, multi-wall carbon nanotubes, double-wall carbon nanotubes, and combinations thereof.
21. The method of Claim 19, wherein the carbon nanotubes comprise nanotubes having diameters less than about 3 nm.
22. The method of Claims 19-20, or 21, wherein the substrate is a fibrous material selected from the group consisting of paper, synthetic polymers, cotton, silk, and combinations thereof.
23. The method of Claims 19-20, or 21, wherein the substrate is currency.
24. The method of Claims 19-22, or 23, wherein the photoluminescence properties are pre-determined qualitatively.
25. The method of Claims 19-22, or 23, wherein the photoluminescence properties are pre-determined quantitatively.
26. The method of Claims 19-24, or 25, wherein the liquid medium is selected from the group consisting of water, organic solvents, supercritical fluids, and combinations thereof.
27. The method of Claims 19-25, or 26, wherein the suspension further comprises a surfactant.
28. The method of Claims 19-26, or 27, wherein the suspension further comprises an additive selected from the group consisting of traditional inks, fluorescent inks, dyes, binders, polymeric material, nanoparticles, magnetic materials, and combinations thereof.
29. The method of Claims 19-27, or 28, wherein the step of applying said nanotube ink to said substrate comprises an application method selected from the group consisting of ink spraying, ink jet printing, flowing ink pen transfer, stamping, and combinations thereof.

30. The method of Claims 19-28, or 29, wherein the liquid medium is removed by an evaporative technique.
31. A method comprising the steps of:
- a) selecting a composition comprising (i) a substrate and (ii) a plurality of carbon nanotubes in contact with said substrate, wherein said carbon nanotubes are operable for undergoing photoluminescence at a pre-determined range of wavelengths;
 - b) irradiating the composition with radiation of a range of wavelengths; and
 - c) detecting luminescence emission at corresponding first van Hove wavelengths in the near infrared.
32. The method of Claim 31, wherein the carbon nanotubes are selected from the group consisting of single-wall carbon nanotubes, multi-wall carbon nanotubes, double-wall carbon nanotubes, and combinations thereof.
33. The method of Claim 31 or 32, wherein the step of irradiating is done with radiation of a range of wavelengths which match second, third, or higher van Hove optical transitions within the carbon nanotubes.
34. The method of Claim 31 or 32, wherein the step of irradiating is done with radiation of a range of wavelengths which match the plasmon resonance optical transitions within the carbon nanotubes.
35. The method of Claims 31-33, or 34, wherein the detecting step is carried out by a process selected from the group consisting of near-infrared camera detection, spectral filtering, and combinations thereof.
36. The method of Claim 35, wherein the near-infrared camera detection comprises the use of a camera selected from the group consisting of an InGaAs camera, a Si camera, and combinations thereof.
37. The method of Claims 31-35, or 36, wherein (a) the substrate is selected from the group consisting of genuine securities, counterfeit securities, and combinations thereof and (b) said method provides a mechanism in which to distinguish whether the substrate is a genuine security or a counterfeit security.
38. The method of Claims 31-35, or 36, wherein the security is currency.

39. The method of Claims 31-35, or 36, wherein (a) the substrate is a currency and (b) said method provides a mechanism in which to differentiate the currency by its bill denomination.
40. The method of Claims 31-35, or 36, wherein said method provides a mechanism in which to spectrally bar code items for non-contact identification purposes.
41. A method comprising the steps of:
- a) providing a plurality of carbon nanotubes with unique, predetermined photoluminescence characteristics; and
 - b) incorporating the carbon nanotubes into articles as optical identifiers to form optically tagged articles.
42. The method of Claim 41 further comprising the steps of:
- a) irradiating the optically tagged articles with EM radiation; and
 - b) detecting photoluminescence from the carbon nanotubes for the purpose of identifying the optically tagged article.
43. The method of Claim 42, wherein the step of irradiating utilizes a source that emits radiation in the visible region of the EM spectrum.
44. The method of Claim 42, wherein the step of irradiating utilizes a source that emits radiation selected from the group consisting of monochromatic radiation and polychromatic radiation.
45. The method of Claim 43, wherein the source is a laser.
46. The method of Claim 42, wherein the step of irradiating utilizes multiple discrete excitation wavelengths.
47. The method of Claims 41-45, or 46, wherein the photoluminescence is in the near infrared region of the EM spectrum.
48. The method of Claim 47, wherein the detecting photoluminescence comprises the use of a camera selected from the group consisting of an InGaAs camera, a Si camera, and combinations thereof.

49. The method of Claims 41-47, or 48, wherein the carbon nanotubes are selected from the group consisting of single-wall carbon nanotubes, multi-wall carbon nanotubes, double-wall carbon nanotubes, and combinations thereof.
50. The method of Claims 41-47, or 48, wherein the carbon nanotubes comprise single-wall carbon nanotubes.
51. The method of Claims 41-47, or 48, wherein the carbon nanotubes comprise nanotubes having diameters less than about 3 nm.
52. The method of Claims 49-50, or 51, wherein at least some of the carbon nanotubes have been chemically functionalized.
53. The method of Claims 49-51, or 52, wherein at least some of the carbon nanotubes have undergone a process to separate them based a characteristic selected from the group consisting of length, diameter, chirality, bandgap, and combinations thereof.
54. The method of Claims 49-52, or 53, wherein the plurality of carbon nanotubes is substantially homogeneous.
55. The method of Claims 49-52, or 53, wherein the photoluminescence of the carbon nanotubes is derived from a unique combination of carbon nanotubes of varying characteristic.
56. The method of Claims 49-54, or 55, wherein the step of incorporating comprises an attachment mechanism.
57. The method of Claims 49-55, or 56, wherein the articles being optically tagged are selected from the group consisting of currency, securities, documents, passports, pharmaceuticals, articles of manufacture, and combinations thereof.
58. The method of Claims 49-55, or 56, wherein the articles are being optically tagged for anti-counterfeiting purposes.
59. The method of Claims 49-55, or 56, wherein the articles are being optically tagged for anti-piracy purposes.
60. The method of Claims 49-55, or 56, wherein the articles are being optically tagged for inventory assessment purposes.

61. The method of Claims 49-55, or 56, wherein the articles are being optically tagged for quality control purposes.
62. A method comprising the steps of:
- a) selecting an article comprising carbon nanotubes;
 - b) irradiating the article with EM radiation so as to effect photoluminescence from any semiconducting carbon nanotubes present; and
 - c) comparing the photoluminescence to photoluminescence characteristics of known carbon nanotube populations for purposes of identification.
63. The method of Claim 62, wherein the carbon nanotubes are operable for undergoing photoluminescence and yielding emission within a second pre-determined photoluminescence characteristic when irradiated with radiation from a region of the EM spectrum selected from the group consisting of visible, ultraviolet, and combinations thereof, and further comprising the steps of:
- a) irradiating the article with a second EM radiation so as to effect a second photoluminescence from the carbon nanotubes, wherein the second EM radiation is different than the first EM radiation; and
 - b) comparing the second photoluminescence to the second pre-determined photoluminescence characteristics for purposes of identification.
64. The method of Claim 63, wherein the second EM radiation has different spectral characteristics than the first EM radiation.
65. The method of Claims 62-63, or 64, wherein the carbon nanotubes are selected from the group consisting of single-wall carbon nanotubes, multi-wall carbon nanotubes, double-wall carbon nanotubes, and combinations thereof.
66. The method of Claims 62-63, or 64, wherein at least some of the carbon nanotubes have been chemically functionalized.
67. The method of Claims 62-63, or 64, wherein the carbon nanotubes comprise single-wall carbon nanotubes.
68. The method of Claims 62-63, or 64, wherein the carbon nanotubes comprise nanotubes having diameters less than about 3 nm.

69. The method of Claims 62-67, or 68, wherein the steps of irradiating are done with EM radiation comprising wavelengths in a region of the EM spectrum selected from the group consisting of visible, ultraviolet, and combinations thereof.
70. The method of Claims 62-68, or 69, wherein the step of irradiating is done with radiation selected from the group consisting of polychromatic radiation, monochromatic radiation, and combinations thereof.
71. The method of Claims 62-68, or 69, wherein the step of irradiating is done with at least one laser source.
72. The method of Claims 62-70, or 71, wherein the photoluminescence comprises emission wavelengths in the near infrared region of the EM spectrum.
73. The method of Claims 62-70, or 71, wherein the step of comparing involves an analysis of the photoluminescence.
74. The method of Claim 73, wherein the analysis is quantitative.
75. The method of Claim 73, wherein the analysis is qualitative.

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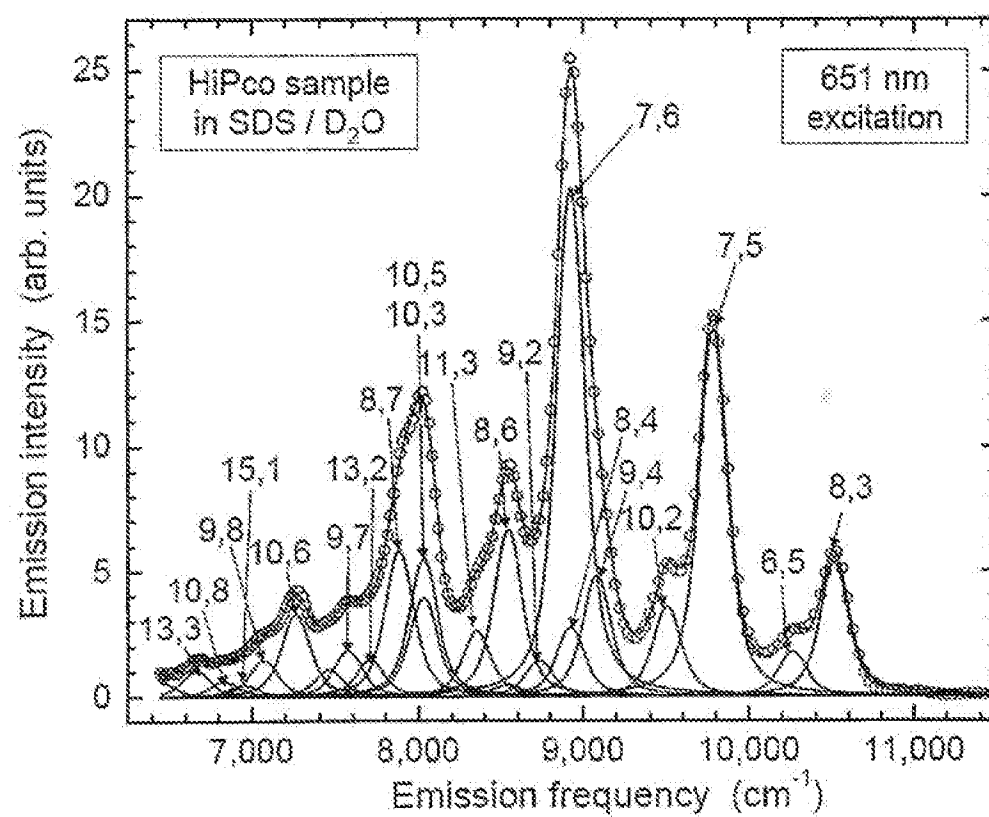
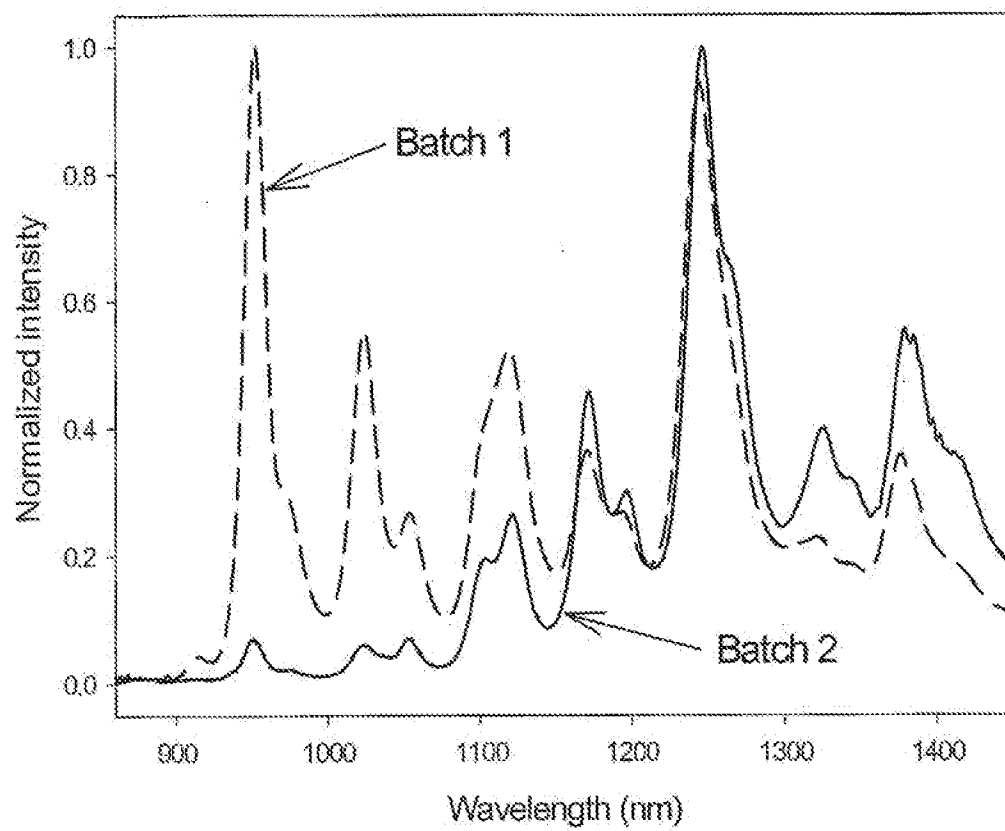


Fig. 1

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*Fig. 2*

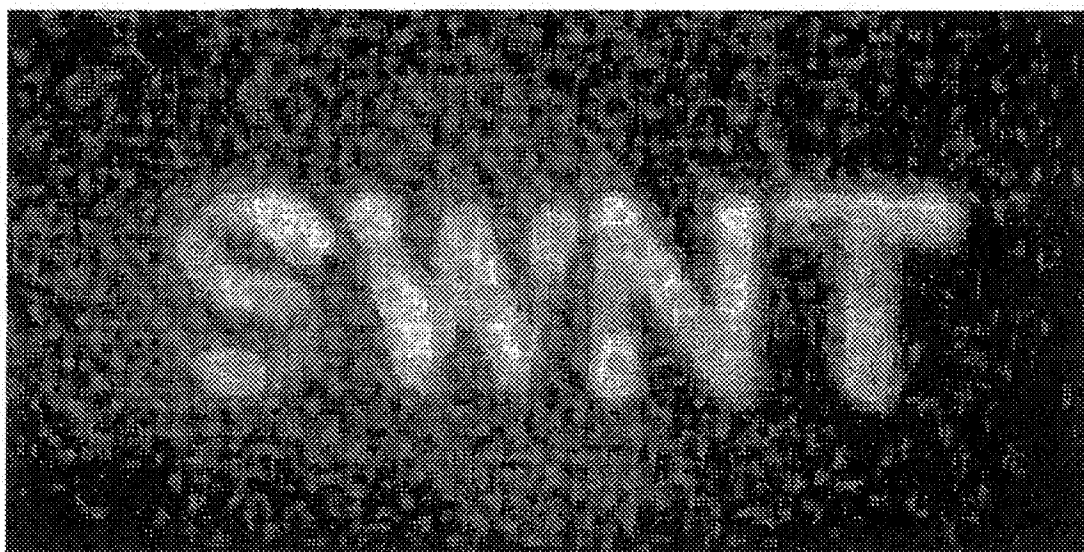
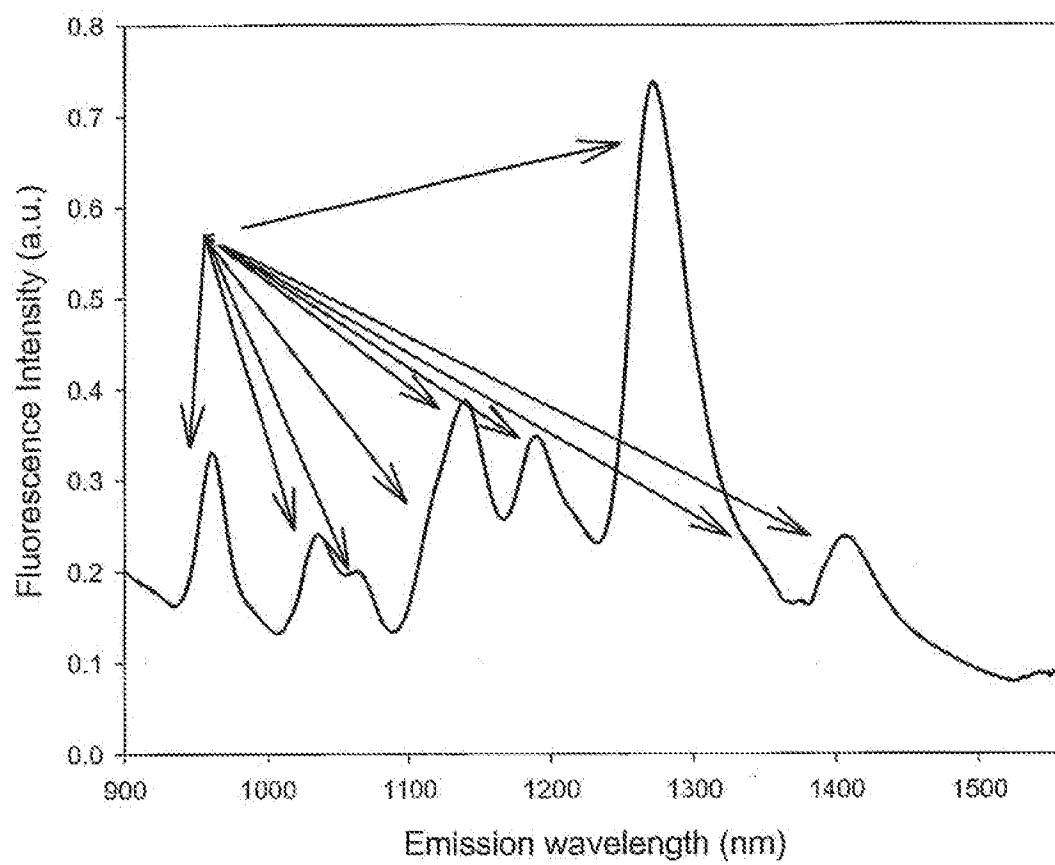
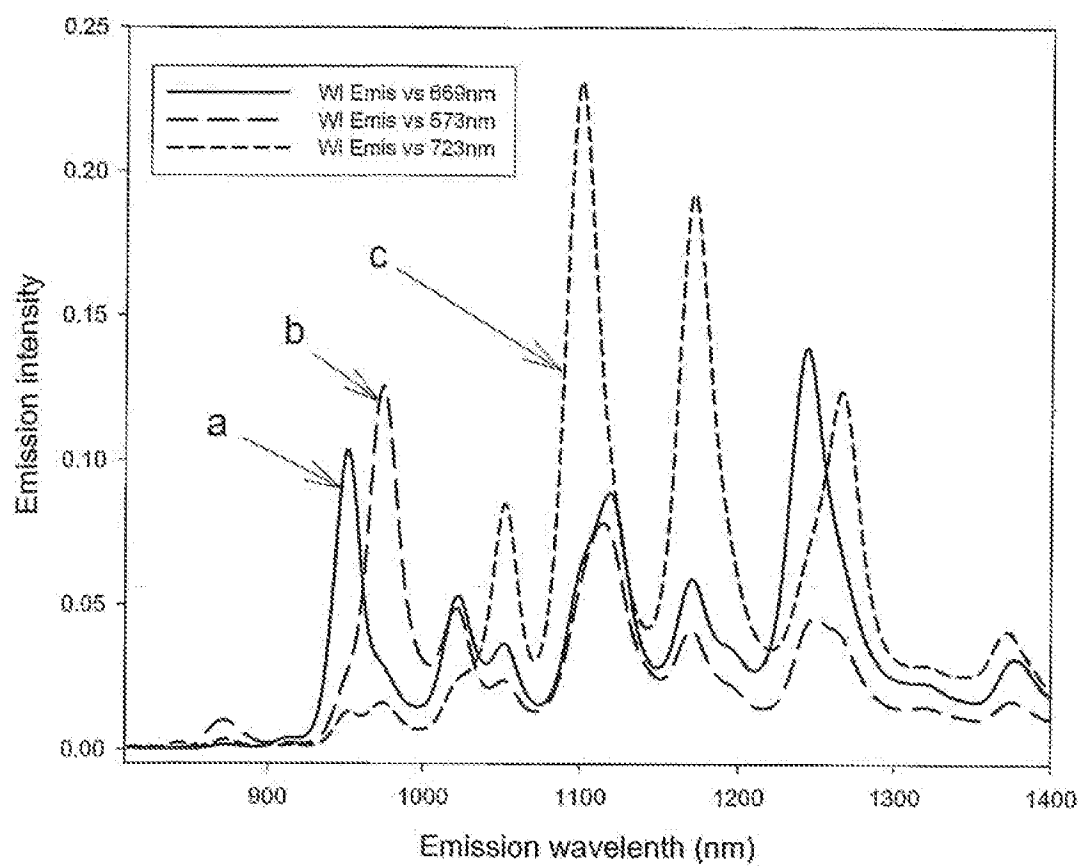


Fig. 3

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*Fig. 4*

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*Fig. 5*